Volatile Acids of Cigar Smoke

Introduction

Although cigarette smoke has been investigated extensively for the presence of volatile acids, no reports have appeared describing similar studies on cigar smoke. The lower aliphatic acids of cigarette smoke have been isolated and identified by several groups of workers. Recently, Izawa and Kobashi (1958) isolated the lower fatty acids from C_1 to C_5 in addition to β-methylvaleric and benzoic acids; identification was made by preparation of crystalline derivatives. In another study, Buyske and his co-workers (1957) reported the presence in cigarette smoke of the fatty acids from C_1 to C_{10} in addition to benzoic acid, using column and paper chromatographic methods of identification. The latter work included quantitative data.

Since cigar tobacco undergoes a method of processing different from that of cigarette tobacco and since no information is available on the volatile acid composition of cigar smoke, a study of such constituents appeared to be of interest. The present report presents qualitative and quantitative data on the major volatile acids of cigar smoke condensate.

Experimental

Collection of Smoke: Cigars were equilibrated for one week at 68 per cent relative humidity and 25° C. before smoking. They were smoked using the automatic smoking machine and experimental conditions

[1]Senior and Junior Research Fellows, respectively, Cigar Manufacturers Association of America.

[2] Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

[3] This ether solution contained only a small amount of the steam-distillable material which was later shown to be phenolic in nature.

described earlier (Schepartz, 1959, 1960). The smoke was collected in traps cooled in acetone-dry ice.

Two popular brands of cigars were smoked: a panatella with all-Havana filler and drawn tuck, and a perfecto with a cut filler of blended domestic tobaccos. Usually, 25-30 cigars yielded sufficient smoke condensate for analysis.

Fractionation of the Condensate: The traps containing smoke condensate were washed successively with ether, absolute methanol and 5 per cent sodium hydroxide solution. The ether extract was then extracted with alkali to remove acidic material. The methanolic solution was made alkaline with 5 per cent sodium hydroxide solution and the solvent evaporated in vacuo. The residue was dissolved in water and extracted with ether to remove neutrals and bases. All the alkaline solutions were then pooled.

The combined alkaline solution was concentrated to a volume of 100 ml, acidified to pH 2.0 with phosphoric acid and steam distilled. One and a half liters of steam distillate were collected and titrated potentiometrically to pH 7.0 with 0.1 N sodium hydroxide to estimate the total steam-volatile acidity. After extraction of the resulting neutralized distillate with ether,[3] the distillate was evaporated to dryness yielding a brown residue of sodium salts.

Silicic Acid Chromatography: The chromatographic procedure of Buyske et al. (1957) was applied to the mixture of sodium salts. However, the silicic acid was unwashed, and the column was larger (2 x 20 cm). The column was prepared by mixing 40 g of silicic acid with 36 ml of 2 M glycine adjusted to pH 2.0 with concentrated hydrochloric acid, slurrying the resulting powder in 200 ml of chloroform and pouring the slurry into the column. A slurry of the

sample and 2 g of silicic acid in 2 ml of glycine solution and 5 ml of chloroform was quantitatively transferred to the column, and the column was successively eluted with 200 ml each of 1, 10 and 25 per cent n-butyl alcohol in chloroform, Finally, an additional 100 ml of the 25 per cent solution was then passed through the column. Ten milliliter fractions were collected and titrated with 0.01 N methanolic sodium hydroxide using bromthymol blue as the indicator. A plot of the elution data indicated two major and two minor peaks (Figure 1). The elution curves for the two brands of cigars were similar to each other and to the data obtained by Buyske et al. (1957) for the volatile acids of cigarette smoke. According to these workers, the first peak contains higher homologues of propionic acid and other acids, the second peak is propionic acid, the third peak is acetic acid and the fourth peak is formic acid.

Identification of Acids: The peaks were chromatographed on paper using several different solvent systems:

(1) 95% ethanol/concentrated ammonia (100:1) (Kennedy and Barker, 1951)

(2) n-butyl alcohol/water/n-propylamine (100:15:1) (Buyske et al., 1957)

(3) t-butyl alcohol/n-butanol/concentrated ammonia (1:1:1) (Schwartzman, 1960)

(4) acetone/water/concentrated ammonia (95:5:1) (Kennedy and Barker, 1951). Spray reagents consisted of a mixture of 50 mg bromphenol blue, 200 mg citric acid, 100 ml absolute ethanol or, in case of the solvent system containing propylamine, of 0.1 per cent ninhydrin in chloroform.

Following the column chromatographic separation, the eluted fractions corresponding to a single peak were pooled, evaporated to dryness,

aken up in water, acidified and steam distilled. The acids were isolated from the distillates as the ammonium or sodium salts and chromatographed. Chromatograms of the ammonium salts of the acids were usually more satisfactory than those of the sodium salts. Unwashed Whatman No. 1 paper[4] was found to be satisfactory in all cases.

The first eluted peak contained four components having the same R_f values as authentic n-butyric, n-valeric, n-caproic and n-heptylic acids. Chromatograms of the second eluted peak gave a single component with R_f corresponding to propionic acid. Unfortunately, the salts of authentic formic and acetic acids failed to separate definitively on paper and differentiation was not possible with the material from the third and fourth peaks, although a single spot having the same R_f as the authentic salts of formic and acetic acids was obtained from each of the two peaks. The residues from the third and fourth peaks were then independently steam distilled after acidification, converted to the sodium salts and examined by infrared spectrophotometry as Nujol mulls. The infrared spectra of the salts prepared from peaks III and IV **(Figure 1)** were identical with those of authentic sodium acetate and sodium formate, respectively.

Results and Discussion

The levels of the major volatile acids obtained from the two brands of cigars by calculation according to Buyske *et al.* are presented in **Table 1.** The milliequivalent values are averages of duplicate runs with the ranges indicated in parentheses. The indicated acids represented about 80-90 per cent of the total volatile acidity; the remainder consisted of unidentified substances most of which were not eluted from columns under the experimental conditions.

The qualitative pattern of the volatile acids was similar to that reported for cigarette smoke (Buyske *et al.,* 1957). For both cigars, acetic acid was the major volatile acid, and combined acetic and formic acid represented over 75 per cent of the total volatile acids (milliequivalent basis). Comparing these data with the published values for cigarette smoke cited above, we conclude that cigar
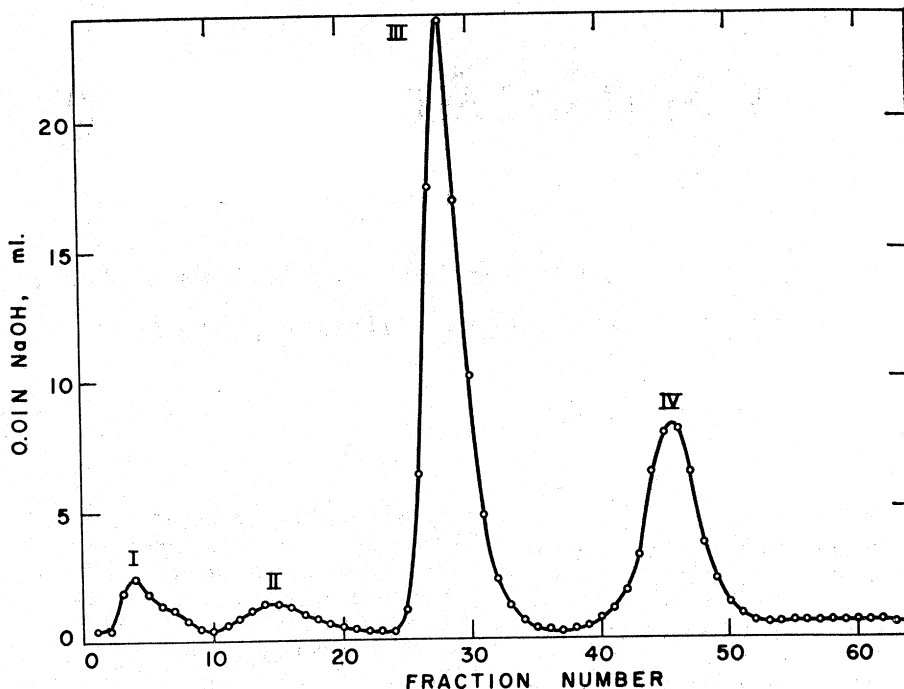
Figure 1. Elution pattern of volatile acids from cigar smoke.

smoke contains about one-third the volatile acidity of cigarette smoke on the basis of mg acid per gram of tobacco smoked.

In considering the possible origins of the volatile acids present in tobacco smoke, the data reported above are perhaps not unexpected. Greater opportunities for losses of volatile material exist in the relatively drastic processes of air-curing and fermentation of cigar tobaccos compared to cigarette tobaccos. These losses probably offset the anticipated higher levels of volatile organic acids which may result from more extensive carbohydrate degradation in the cigar tobacco leaves.[5] However, such complicating factors as differences in pH of cigar and cigarette tobaccos and smoke render difficult a conclusive explanation of the observed patterns of volatile acids present in the smoke.

Summary

Volatile acids were removed from cigar smoke condensate by solvent extraction and steam distillation. Fractionation of the individual acids was achieved by partition chromatography on silicic acid. Acetic and formic acids were found to comprise about 75 per cent of the total volatile acidity with acetic acid predominating. Cigar smoke contains smaller amounts of volatile acids than those reported for cigarette smoke on the basis of weight of tobacco smoked.

Table 1. Volatile acids in cigar smoke condensate

	Panatella			*Perfecto*		
	meq*	mg*	mg**	meq*	mg*	mg**
Formic	1.43 (±0.19)	65.8	12.1	1.29 (±0.11)	59.3	10.9
Acetic	2.90 (±0.34)	174	32.0	2.60 (±0.44)	156	28.6
Propionic	0.34 (±0.03)	25.2	4.63	0.35 (±0.02)	25.9	4.74
Butyric and higher	0.52 (±0.13)	53.0†	9.75	0.50 (±0.05)	51.0	9.34

* Amounts per 100 cigars smoked. Panatellas weighed 8 g and 68 per cent of cigar was smoked; perfectos weighed 7 g and 78 per cent of cigar was smoked.

** Amounts per 100 g of tobacco smoked.

† Assuming mol wt of 102.

Literature Cited

Bradford, J. A., E. S. Harlow, W. R. Harlan and H. R. Hanmer, "Nature of Cigaret Smoke." *Industrial and Engineering Chem.* 29:45-50 (1937).

Buyske, D. A., P. Wilder, Jr., and M. E. Hobbs, "Volatile Organic Acids of Tobacco Smoke." *Anal. Chem.* 29:105-108 (1957).

Izawa, M. and Y. Kobashi, "Some Volatile Acids and Esters of Cigarette Smoke." *Bull. Agricultural Chem. Soc. Japan* 22:47-53 (1958).

Kennedy, E. P. and H. A. Barker, "Paper Chromatography of Volatile Acids." *Anal. Chem.* 23: 1033-1034 (1951).

Schepartz, A. I., "The Chemistry of Cigar Smoke. I. An Automatic Smoking Machine for Cigars." *Tobacco Science* 3: 144-147 (1959).

Schepartz, A. I., "The Chemistry of Cigar Smoke. II. Some Components of the Neutral Fraction." *Tobacco Science* 4: 12-16 (1960).

Schwartzman, G., "Separation and Identification of Sodium Salts of C_2 to C_5 Volatile Fatty Acids by Paper Chromatography." *J. Assoc. Off. Agr. Chem.* 43: 428 - 430 (1960).

Quin, L. D., W. George and B. S. Menefee, "Some Semiquantitative Gas Chromatographic Studies on the Organic Acids of Tobacco and Its Smoke." *J. Assoc. Off. Agr. Chem.* 44: 367-373 (1961).